CEMENT AND LIME MANUFACTURE

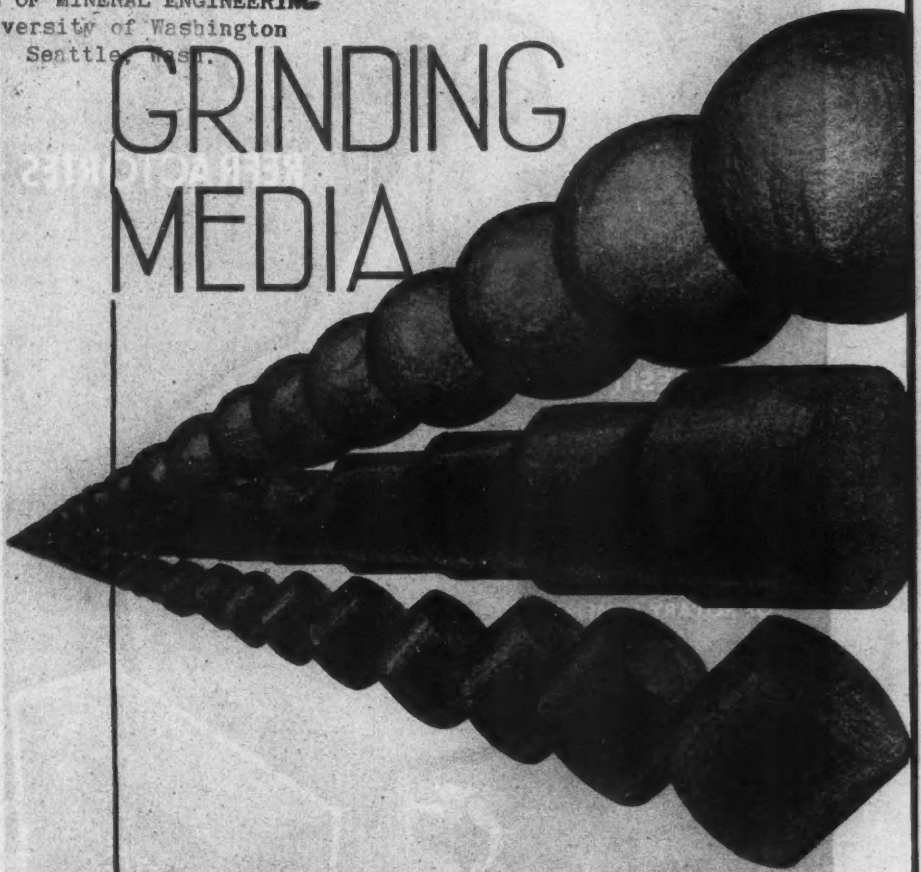
691.5
CEM

LIBRARY
UNIVERSITY OF WASHINGTON
22 DEC 1948

VOL. XXI. No. 6 — NOVEMBER 1948 — PRICE 1/- ALTERNATE MONTHS

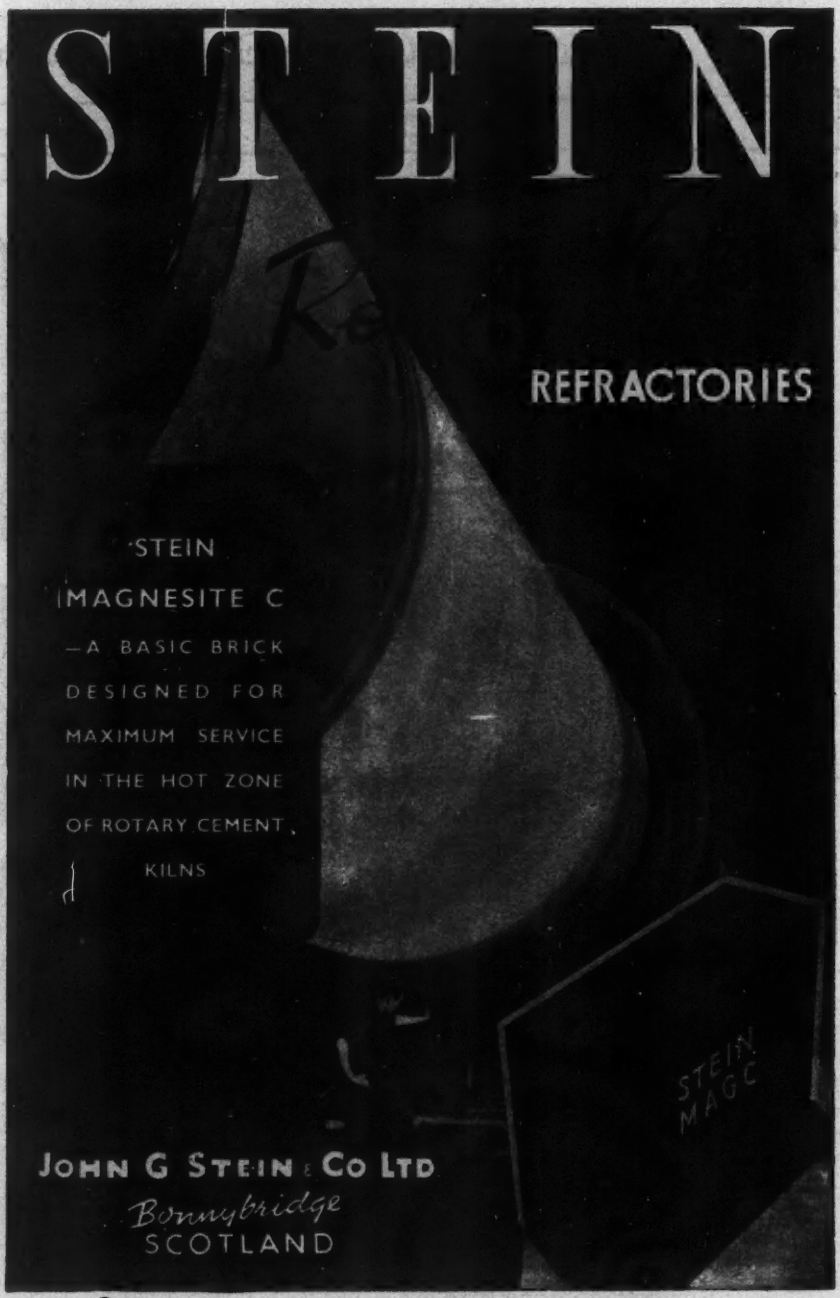
LIBRARY COPY
SCHOOL OF MINERAL ENGINEERING
University of Washington
Seattle, Wash.

GRINDING MEDIA



HELIPEBS LTD
PHONE: GLOUCESTER 4051
GRAMS: HOLPRESS GLOUCESTER
PREMIER WORKS
GLOUCESTER

PUBLISHED BY CONCRETE PUBLICATIONS, LTD., 14, DARTMOUTH STREET, LONDON, S.W.1


STEIN
REFRACTORIES
STEIN
IMAGNESITE C
—A BASIC BRICK
DESIGNED FOR
MAXIMUM SERVICE
IN THE HOT ZONE
OF ROTARY CEMENT
KILNS
STEIN MAGC
JOHN G STEIN & CO LTD
Bonnybridge
SCOTLAND

CEMENT AND LIME MANUFACTURE

PUBLISHED ALTERNATE MONTHS. PRICE 1/- A COPY. ANNUAL SUBSCRIPTION 6s. POST FREE.

PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
14 DARTMOUTH STREET, LONDON, S.W.1

TELEPHONE: WHITEHALL 4581.
TELEGRAPHIC ADDRESS
CONCRETIUS, PARL. LONDON.

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & LIME MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME XXI. NUMBER 6 NOVEMBER, 1948

Expansion of Cement Measured by Autoclave Tests.

By LÉON BLONDIAU (Director of S.A. des Ciments de Thieu, Belgium).

THE inclusion of the autoclave test in the United States specifications for Portland cement has made it necessary for cement manufacturers in Belgium, whose products are exported to the United States, to examine their cements by this method. For this reason many tests have been made in the laboratories of S.A. des Ciments de Thieu, the objects being (1) to determine the uniformity of the results obtained by this method and by different testers, and the effect of the size of the specimens; (2) to examine the influence on the expansion in the autoclave of the addition of gypsum, quenching of the clinker, and aeration; (3) to compare the results obtained by the hot-pat test, the Le Chatelier test, the test in which the specimens are exposed to water vapour at 100 deg. C., and the autoclave test, and, more importantly, to examine the influence of the content of free lime, magnesia, and tricalcium-aluminate; (4) to study the influence of the fineness and to determine a suitable fineness for a cement to be stable in the autoclave having regard to other factors in the manufacture; (5) to study the stability in the autoclave of slag-cements, the influence of the addition of slag on potentially-expansive clinkers, and the increase of stability of Portland cements by the addition of pozzolana.

Effect of Different Testers.

The first series of tests was carried out strictly in accordance with the method described by the American Society for Testing Materials, using apparatus made in the United States. One man made specimens that were tested simultaneously in the autoclave, and the same man then made specimens with cement that had been stored for 48 hours in an air-tight box. Forty-eight hours after, another man made identical tests. The difference in the results of the tests of specimens made by one man was less than 0·05 per cent., and the difference between those made by the two men was even less, being about 0·02 per cent.

The expansion of 5-in. specimens was greater than that of the 10-in. specimens specified in United States standards, but as the difference did not exceed 0·2 per

cent. the smaller specimens can be used with assurance for routine examination of expansion in an autoclave.

Effects of Gypsum, Quenching and Aeration.

The influence on expansion of the addition of gypsum is not less important than its effect on the setting properties and strength of the hardened paste. The limitation of the SO_3-content of Portland cement is to prevent delayed expansion by the reaction of the gypsum with the aluminates in forming calcium-sulpho-aluminate, a reaction which the cold-pat test is intended to disclose. The influence of gypsum is also disclosed by the Le Chatelier test. From *Fig.* 1, which gives a comparison between the expansion measured by the autoclave test and the Le Chatelier test for various amounts of gypsum, it is seen that gypsum contents exceeding 4 per cent. had little effect on expansion. In the tests represented by *Fig.* 1 the effects of the reactions consequent upon the heat developed during

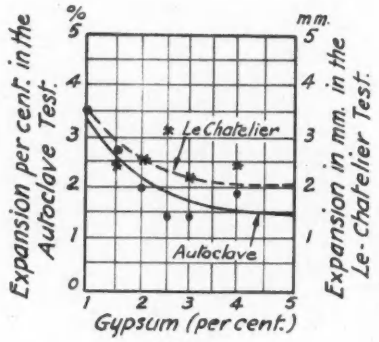


Fig. 1.

grinding were eliminated by grinding the clinker in a laboratory mill, and the only variable was the content of gypsum.

Watering the incandescent clinker as it is discharged from the kiln is not a scientific method of cooling, but as it is an easy method many works will desire to retain it, especially as this method decreases the expansion as measured in an autoclave, which is much more important when the expansion is great. Likewise aeration, by the hydration and carbonation of the free lime, causes a decrease in the expansion and consequently results in a decrease of expansion in the autoclave. The action is much greater and more rapid if the ambient conditions are humid. The improvement of stability by quenching and aeration has led some manufacturers to adopt these means to improve imperfectly or irregularly calcined clinkers, but such processes are only palliatives.

Comparison of Methods of Testing Expansion.

In the third series of tests, 117 commercial clinkers were tested. It was thought better to examine clinker rather than cement, as stable clinker can only produce

stable cement, although a stable cement can, by virtue of the action of the water liberated by gypsum, also be obtained from an unstable clinker. Each sample of clinker was mixed with 3 per cent. of gypsum, the object being to obtain a cement having an SO_3-content of 1·5 per cent., which is below the maximum of 2 per cent. required by United States specifications, and to reduce the influence of the gypsum on the delayed instability. The chemical analyses were made by the ordinary methods, and the proportion of free lime was determined by the glycerine-alcohol method. The constitution of the clinker was calculated by the formula of Mr. Bogue and expressed relative to that of a slowly-cooled clinker in a state of complete equilibrium. Because of the influence of the glass on the stability it is admitted that the real constitution has not been determined, but it must be borne in mind that the practical purpose of the tests was to determine,

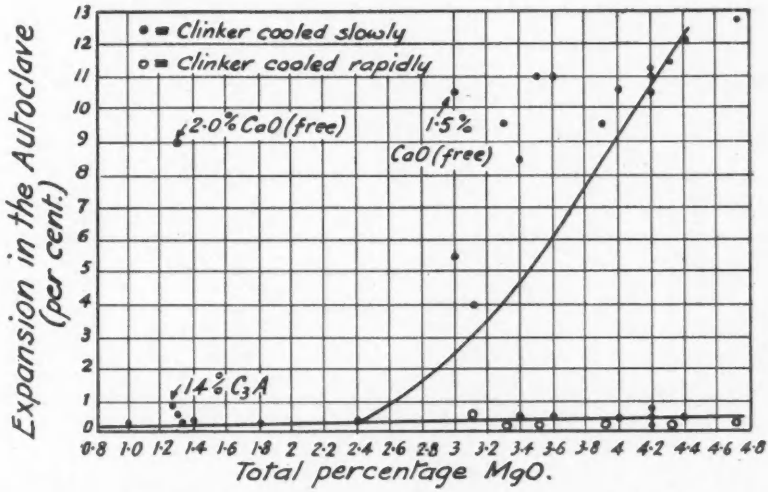

• = Clinker cooled slowly
o = Clinker cooled rapidly
2·0% CaO (free)
1·5% CaO (free)
14% C3A
Expansion in the Autoclave (per cent.)
Total percentage MgO.
0·8 1·0 1·2 1·4 1·6 1·8 2 2·2 2·4 2·6 2·8 3 3·2 3·4 3·6 3·8 4 4·2 4·4 4·6 4·8
0 1 2 3 4 5 6 7 8 9 10 11 12 13

Fig. 2.—Relation Between the Magnesia Content and Expansion in Autoclave Tests. (5 hours at 215 deg. C.).

in an existing works without alteration to the plant or the raw materials, the variables affecting the phenomenon of delayed expansion. The variation from which it is possible most easily to obtain results, for a fineness equal to that of coarse grinding, is the chemical composition. Fig. 2 shows the effect of the MgO-content on the expansion of commercial cements in the autoclave. The expansion is very small if the clinker is cooled rapidly, but for MgO-contents exceeding 2·5 per cent. the expansion is great if cooled slowly.

COMPARISON OF LE CHATELIER AND AUTOCLAVE TESTS.—The cements used for these tests were ground to about the same degree of fineness. The content of MgO did not exceed in any case 1 per cent.; it was generally about 0·6 per cent., and can be considered as practically constant. With such low values

MgO can be excluded as a variable in these tests. If the expansions are plotted in the order of the expansion as measured by the Le Chatelier apparatus, two curves can be drawn to show the average results of the autoclave and Le Chatelier tests. The expansions shown by the autoclave test are generally less than 0·5 per cent. if there is no expansion recorded by the Le Chatelier test, but, when the latter exceeds 0·25 mm., the expansions shown by the autoclave test generally attain 0·5 per cent. When the expansion by the Le Chatelier test exceeds 0·5 mm., and particularly when it attains 1 mm., the expansion in the autoclave grows rapidly to such a degree that generally the specimens disintegrate. Although there is therefore no true relation between the results of the two methods, it can be concluded that the Le Chatelier test does not disclose the

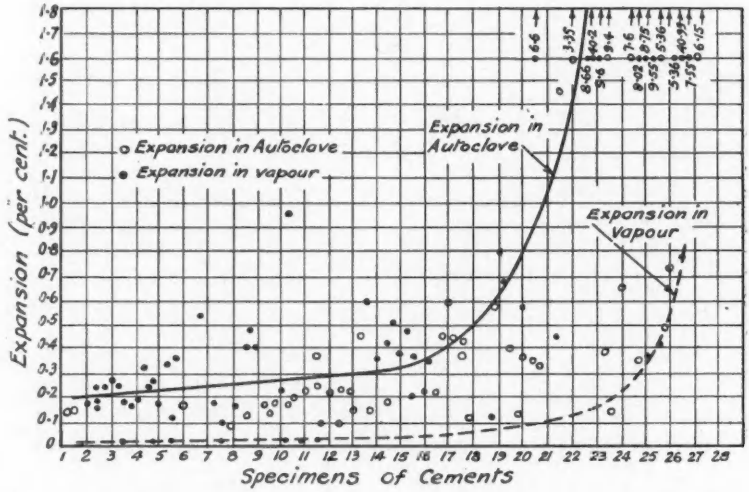


Fig. 3.—Comparison of Expansion in the Vapour Test and in the Autoclave.

potential expansion, that the maximum expansion of about 5 mm. required by some specifications apply to cements that are highly expansive in an autoclave, and that a cement may satisfy the autoclave test only if the expansion by the Le Chatelier test is below 0·25 mm.

COMPARISON OF EXPANSION IN VAPOUR AND IN THE AUTOCLAVE.—The tests in vapour at 100 deg. C. were made in accordance with the method specified by the American Society for Testing Materials, and to enable exact observations to be made some of the specimens were 10 in. long. The cements tested are, in *Fig.* 3, placed in the order of expansion as shown by the vapour test, and the corresponding expansions in the autoclave are given. The expansion in vapour is much less than that measured in the autoclave, and, like the Le Chatelier test, the vapour test cannot measure the potential expansion of a cement. The limit

of 0·5 per cent. expansion required in the autoclave test is exceeded when expansion in the vapour test exceeds 0·075 per cent.

In view of the foregoing, it is not an exaggeration to conclude that few commercial cements will satisfy the autoclave test unless considerable modifications are made in the manufacture.

Chemical Composition and Expansion in the Autoclave.

The variation in the results of tests does not permit a relation between expansion in the autoclave and the sum of the expansive constituents (free lime + MgO + C_3A) to be established. It is possible that the expansion increases as this sum increases.

FREE LIME AND TRICALCIUM-ALUMINATE.—*Fig.* 4 shows the relation between expansion in the autoclave and the free-lime content without taking into account

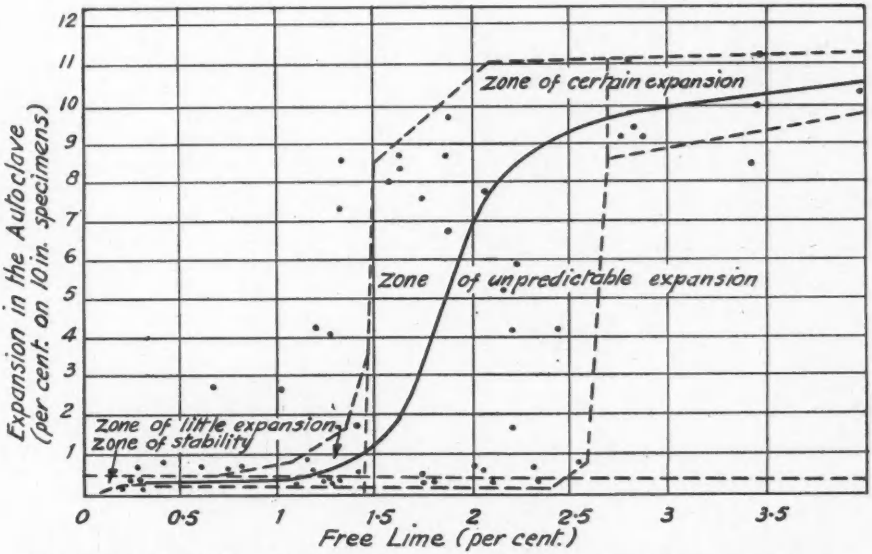


Fig. 4.—Relation Between Expansion in the Autoclave and the Free-lime Content.

the eventual action of the MgO and C_3A. It can be stated that cements with even less than 0·5 per cent. of free lime have an expansive tendency. The diagram can be divided into four zones, namely: (1) A stable zone in which the expansion is generally less than the limit of 0·5 per cent., and which includes cements in which the content of free lime is less than 0·7 per cent. (2) A zone of little expansion in which the expansion remains about 0·5 per cent. but with a marked tendency to exceed this amount; this zone includes cements having a free-lime content of 0·7 per cent. to 1·5 per cent. (3) A zone in which the expansion cannot be predicted, and in which are included cements having a free-lime content of 1·5 per

cent. to 2·5 per cent.; the expansions for some cements are about 0·5 per cent., while for others this limit is exceeded and the specimens may even disintegrate. (4) A zone of certain expansion, in which cements having 2·5 per cent. or more of free lime are disintegrated during the test. Examination of *Fig.* 4 does not permit, however, the influence of free lime to be precisely established. Each zone contains a number of exceptional results which it is presumed are due to other variables, but the only variables than can affect expansion are the contents of magnesia and tricalcium-aluminate. A very low content of MgO permits exclusion of this variable in the present case. Thus the effect of the content of C_3A must be considered, as in *Fig.* 5.

Fig. 5 (*a*) relates to cements containing from 0·3 per cent. to 0·37 per cent. of free lime and from an examination of the curve it can be concluded that

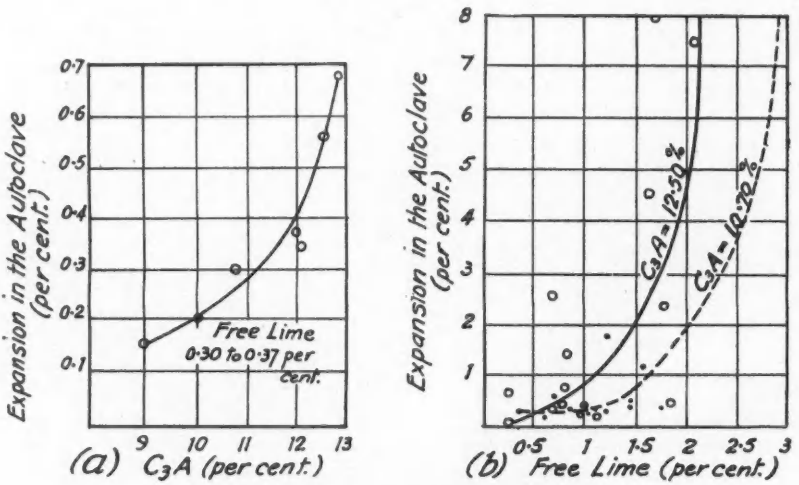


Fig. 5.—Influence of Calcium Aluminate.

even with a low free-lime content the expansion grows rapidly as the C_3A-content increases, and a content of C_3A of 12 per cent. seems to be the limit. *Fig.* 5(*b*) shows the variation of expansion in the autoclave in relation to the free-lime content for C_3A-contents of 12·5 per cent. and 10·7 per cent., and that the smaller the content of C_3A the more susceptible is the expansion to variation in the free-lime content. In the present tests it appears that the delayed expansion of a cement having a C_3A-content of 10·7 per cent. is only accidental for free-lime contents of 1·6 per cent. and upwards.

GLASS CONTENT.—The content of vitreous phase, as calculated by the formula of Dr. Lea and Dr. Parker, was compared with the expansion of the cements tested in the autoclave. The results are given in *Table* I, from which it is seen that the free-lime content increases as the glass content decreases, and that it is

difficult to obtain a clinker that has a glass content of less than 22 per cent. and a low free-lime content. For a glass content of less than 22 per cent. the difficulty of attaining stability in the autoclave is explained by the higher free-lime content. A glass content of from 22 per cent. to 24 per cent. seems to be the amount which should not be exceeded. With a glass content exceeding 24 per cent. the difficulty increases rapidly, and this is explainable if it is considered that cements having a glass content of 22 per cent. to 24 per cent. are those having a C_3A-content of 10·4 per cent. (as calculated by the formula of Mr. Bogue), and that in cements having higher glass contents the proportion of C_3A is greater. The increase of the glass content is due, as indicated by the ratio of C_3A to C_4AF, to the larger proportion of C_3A, and it is possible to predict the favourable influence of the tetracalcium-ferroaluminate. It follows that, for a glass content of 22 per cent. to 24 per cent., the most favourable C_4AF-content for a cement to be stable in the autoclave is such that the ratio of C_3A to C_4AF is between 1·00 and 1·05.

From the third series of tests it can be concluded that to ensure that a cement

TABLE I.

Vitreous phase (per cent.)	Cements stable in the Autoclave.						Cements unstable in the Autoclave.					
	Percentage of cements tested.	chemical characteristics.				Expansion in the Autoclave (per cent.)	Percentage of Cements tested	chemical characteristics				Expansion Autoclave (per cent.)
		C_3A per cent.	C_4AF per cent.	$\frac{C_3A}{C_4AF}$	Free Lime per Cent.			C_3A per cent.	C_4AF per cent.	$\frac{C_3A}{C_4AF}$	Free Lime per cent.	
less than 22	44	9·3	8·4	1·11	1·40	0·40	56	9·7	8·2	1·18	2·3	6·3
22 to 24	63	10·4	8·1	1·28	0·91	0·30	37	10·6	8·4	1·26	2·1	6·3
24 to 26	39	11·5	8·5	1·35	1·12	0·34	61	12·0	8·4	1·42	1·7	4·4
more than 26	33	13·2	8·5	1·55	0·86	0·38	67	13·2	8·7	1·51	1·0	3·2

produced in a rotary kiln will be stable in the autoclave, it is important that the C_3A-content be between 10 per cent. and 11 per cent., that the ratio of C_3A to C_4AF be between 1·00 and 1·05, and that the free-lime content be less than 1 per cent. The glass content will then be 22 per cent. to 24 per cent. by weight of the clinker.

Fineness.

Even with the most favourable contents of free-lime and C_3A, large and inconsistent expansions in the autoclave were experienced. Thus one cement having 10·95 per cent. of C_3A and 1·39 per cent. of free-lime had an expansion of 1·76 per cent., another cement with the same C_3A-content and a free-lime content of 1·45 per cent. had an expansion of 0·51 per cent., and a third cement, having the same composition as the second, had an expansion of only 0·39 per cent. It was thus necessary to conduct research to ensure the production of a stable cement, and in particular the effect of fineness was studied. Nine clinkers of different compositions were ground with 4 per cent. of dry gypsum to finenesses varying

from 3,400 sq. cm. to 1,700 sq. cm. per gramme. The fineness was expressed as the residue in a Mayntz and Petersen flourometer, and as the specific surface determined by a Wagner turbidimeter. A relation between the results of the two methods was established.

Fig. 6 shows the relation between fineness and expansion in the autoclave. It appears that potentially unstable cements become stable if they are sufficiently fine, and that to avoid any expansion it is necessary to have a specific surface of not less than 3,000 sq. cm. per gramme (see cement C). However, some cements attained stability with less fineness, for example, 2,000 sq. cm. to 2,500 sq. cm. per gramme for cements A, B, D, and G, and even 1,500 sq. cm. per gramme for cements E and H. But the fact that cements of identical fineness

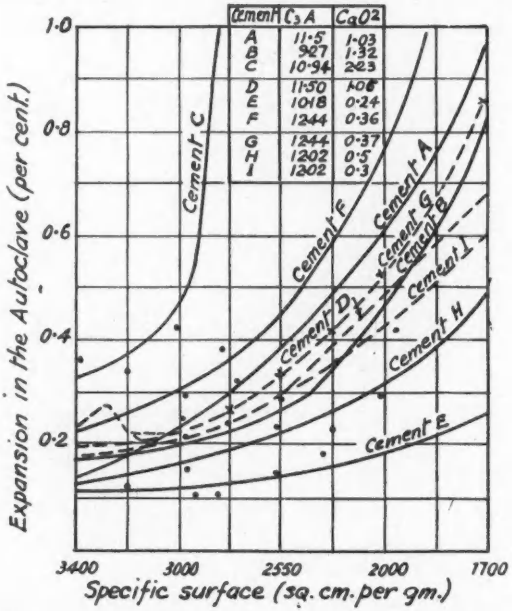


Fig. 6.—Influence of Fineness on Expansion in the Autoclave.

had different expansions shows that fineness is not the principal variable. Moreover, to establish stability in the autoclave by fineness alone leads to other grave difficulties, such as the excessive shrinking of a concrete made with an extremely fine cement.

Thus it was necessary to consider the composition of stable cements having the smallest specific surfaces. *Fig.* 6 shows that stability is attained (1) if the C_3A-content is between 9·3 per cent. and 10·2 per cent., the free-lime content is between 1·3 per cent. and 0·27 per cent., and the fineness is between 1,800 sq. cm. and 2,000 sq. cm. per gramme, or (2) if the C_3A-content is between 11·5

LIBRARY COPY
SCHOOL OF MINERAL ENGINEERING
University of Washington
Seattle, Wash.

per cent. and 12·5 per cent., the free-lime content between 1·0 per cent. and 0·5 per cent., and the fineness 2,550 sq. cm. per gramme.

It seems to be important to adopt the fineness that gives the least shrinkage and to modify the chemical composition accordingly. Some tests were therefore made to establish the relation between shrinkage and expansion in the autoclave for cements of different finenesses. It was found that small expansions corresponded to the least shrinkage, and the least shrinkage seemed to be obtained with stable cements having a fineness of 2,550 sq. cm. to 2,075 sq. cm. per gramme. Such a fineness is obtainable with the machinery in use and produces a cement having ordinary setting properties and strengths equivalent to those required for rapid-hardening Portland cements. The chemical composition of such a cement must be: C_3A, 10 per cent. to 11 per cent.; free lime, not more than 1 per cent.; ratio of C_3A to C_4AF, 1·0 to 1·05.

Thus the fourth series of tests confirms the conclusions drawn from the third series, and demonstrates that the manufacture of cements having low potential expansions is not simple. Although cements complying with the Le Chatelier test give satisfaction in practice, cements supplied in accordance with the specifications of the United States must comply with the autoclave test, and consequently the properties of such cements must be considerably altered. For example, to comply with this test, there must be practically no expansion registered by the Le Chatelier apparatus, and other properties, such as the chemical composition, the fineness, and the amount of gypsum to be added, should be as described in the foregoing. It seems that the alterations necessary to ensure that a Portland cement complies with the autoclave test have a favourable effect on the other properties of the cement.

Blastfurnace-Slag Cement.

Blastfurnace-slag Portland cements should be better able to conform to the autoclave test because of their lower content of free-lime, the vitreous nature of the slag, and the combination of active silica with the lime liberated during setting. A number of commercial blastfurnace-slag cements was tested, most of which contained about 70 per cent. of slag and 2·5 per cent. of SO_3, and had a specific surface of about 2,100 sq. cm. per gramme. The expansion in the autoclave was very little, or none, or even negative, varying from +0·55 per cent. to −0·006 per cent.

To ensure that these results were not due to the clinkers from which the blastfurnace-slag cements were made being themselves stable in the autoclave, other tests were made, using clinkers that showed expansion in the autoclave, and to which successive proportions from 10 per cent. to 100 per cent. of granulated slag were added. Five per cent. of dry gypsum was added in each case, and the fineness of the mixture was between 2,200 sq. cm. and 2,400 sq. cm. per gramme. It was found that a small addition of slag (5 per cent. to 10 per cent.) was sufficient for the delayed expansion to fall below 0·4 per cent. When the proportion of slag was 75 per cent., the specimens in the autoclave contracted.

Thus it is concluded that blastfurnace-slag Portland cements have perfect stabilities in the autoclave, and are free from cracking due to the expansion of

the free lime, periclase, and crystalline C_3A. Other factors may, however, cause a change in volume of a cement pat, one of which is the ambient humidity. Some tests are now being made in the laboratories of S.A. des Ciments de Thieu to investigate this problem.

Sulphate Cements.

To confirm the harmlessness, as regards delayed expansion, of even large amounts of MgO dissolved in the vitreous phase, tests were made with a basic blastfurnace-slag which had been quickly cooled and of which the MgO-content was 13·50 per cent. The percentages of other constituents were SiO_2, 27·50; Al_2O_3, 12·50; Fe_2O_3, 4·15; CaO, 37·55; S, 1·45; and SO_2, 0·46. To a mixture comprising 70 per cent. slag and 30 per cent. Portland cement clinker, 5 per cent. of gypsum was added; to this specimen of blastfurnace-slag cement 13 per cent. of gypsum was added to produce a supersulphate cement. The respective expansions of two cements were: Le Chatelier cold-water test, 5 mm. and 3 mm.; Le Chatelier boiling-water test, 1 mm. and 1 mm.; autoclave test, 0·003 per cent. and 0·002 per cent. The results show good agreement between the methods of testing, and this is confirmed by tests with slags having an MgO content of 10·5 per cent.

Pozzolana Cements.

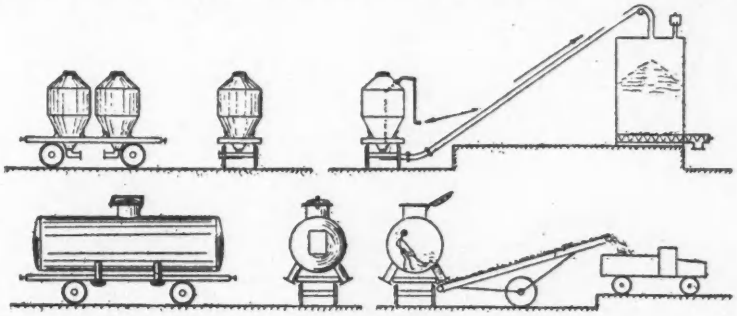
The effect of the addition of pozzolana on delayed expansion was examined by tests on expansive clinkers to which had been added different proportions of pozzolanas from Auvergne and Kieselguhr. Although less marked than the action of basic slags, the addition of these pozzolanas in the proportion of 20 per cent. caused a considerable improvement in stability. It is probable that even better results would have been obtained if a more active pozzolana, such as Santorin earth, had been used.

Exceptional Performance of a Kiln.

A KILN, 325 ft. long, was run without stopping at the works of the Ponce Cement Corporation, Puerto Rico, for a few days in excess of one year during which time the average daily production was 272 tons compared with the rated capacity of 250 tons. In describing this performance, Mr. C. L. Cintron states in "Rock Products" for August, 1948, that in his opinion radiant heat is more beneficial to the burning of clinker than direct flame, because the process of fusion is less rapid and balling and clinker rings are avoided. With a long burning zone and a long narrow flame the clinkering is more controllable, as it is done gradually and more slowly. At the works in question it is the practice for the burner pipe to be capable of being moved about 5 ft. into the kiln. As soon as a ring starts to form the pipe is pushed in so that the flame plays directly on the ring, causing it to crumble. A kiln velocity of 100 revolutions per minute is recommended, since at high speed the slurry is dried and prepared for the calcining zone more quickly. The risk of balling is less. The surface of clinker exposed to the heat changes more rapidly, inducing more uniform burning, and there is insufficient time for magma to form.

Transport of Cement in Bulk.

Two types of wagons designed in Germany for the transport of cement in bulk by railway are shown in the accompanying illustrations, which are taken from a recent number of "Die Bauwirtschaft." On one type there are two cylindrical containers, holding about 26 tons of cement, from which the cement is forced by



compressed air along pipes to a silo fitted with an air-release valve. The second type is a tank wagon, which is made in two sizes; a wagon with two axles, as illustrated, contains about 24 tons of cement and one with four axles contains 38 to 45 tons. The cement is discharged through chutes on to a belt conveyor, the discharge being assisted by hand when necessary.

A Resinous Admixture for Cement.

A RESIN, patented by the Hercules Powder Co. and which is claimed to improve certain properties of cement, is described in the abstract of patent No. 572,817 as follows. A soap of a pine wood resin, which is substantially insoluble in petroleum hydrocarbons, is mixed with cement, mortar, gypsum plaster, lime, pozzolana, or the like, either as a grinding aid during manufacture or immediately before mixing. This is stated to produce a reduction in specific gravity, to facilitate grinding, mixing and positioning, to reduce water-absorption, and to increase resistance to attack by weather and de-icing chemicals. The resin is obtained by treating pine wood, after extraction of the turpentine and pine oil, with a coal-tar hydrocarbon and treating the residue with a petroleum hydrocarbon such as petroleum or with a mixture thereof and furfural. The petroleum-insoluble resin is separated and is saponified by either the hot or cold method. Preferably, the pulverized resinous material is dispersed in cold water by means of a small proportion of alkali, a solution of casein in sodium hydroxide, sodium oleate, sodium alginate, sulphonated higher alcohols, sulphonated naphthalenes, or bentonite, or by mechanical dispersion, and concentrated alkali solution is then added; alternatively, the dry resinous material may be added to the alkali solution. The saponified material may be used in proportions of from 0·005 per cent. to 0·3 per cent. and preferably about 0·04 per cent. by weight of the cement.

Developments in the Cement Industry on the Continent.

Flotation Plant in Scandinavia.

Fig. 1, showing flotation cells in a Continental cement works, is from a recent number of "Rock Products," wherein it is stated that one cement works in Sweden and one in Finland use the flotation process for separating the raw materials.

A Floating Washmill.

In the same journal Mr. G. Albertus and Mr. B. R. Jacobsen state that a novel process on the Continent is the treatment of the clay in a washmill, 15 ft.

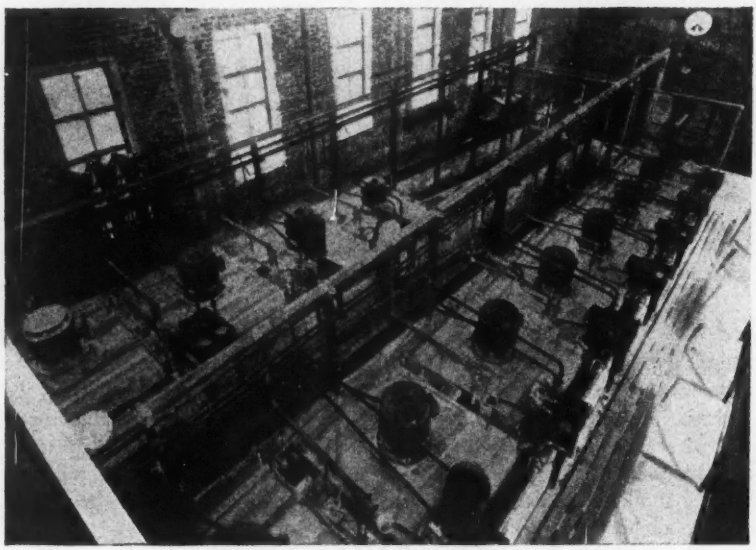


Fig. 1.—Flotation Cells.

diameter, placed on a barge floating in a flooded clay-pit (*Fig.* 2). There are three such installations, the hourly capacity of the largest of which exceeds 40 tons of dry material. The clay slurry is pumped from the barge to the cement works.

Measuring the Viscosity of Slurry.

Among other recent innovations on the Continent is a rotating continuously-acting slurry viscometer which shows the consistency of the slurry so that irregularities can be corrected at once. An electrical acoustic apparatus for measuring the level of the material in wet and dry mills is another development.

Preheaters.

The war-time necessity to reduce the consumption of fuel has led to several existing and new kilns being fitted with slurry preheaters instead of separate preheaters. It is said that, with 36 per cent. of water in the slurry, kilns so equipped have a heat consumption as low as 900,000 B.Th.U. per barrel of clinker (that is about 1300 kg.-cal. per kilogramme). It is found that the preheater causes only a slight increase in the alkali-content of the clinker and a reduction in the amount of dust in the gases discharged from the kiln. Owing to the increased amount of alkali in the dust precipitated in the preheater (the dust may contain about 75 per cent. of alkali salts) the dust can be used as a fertiliser.

New Dry-Process Plants.

Although the wet process is that most commonly adopted, the dry process, which was used in Italy, Spain, and Yugoslavia before the war, has developed

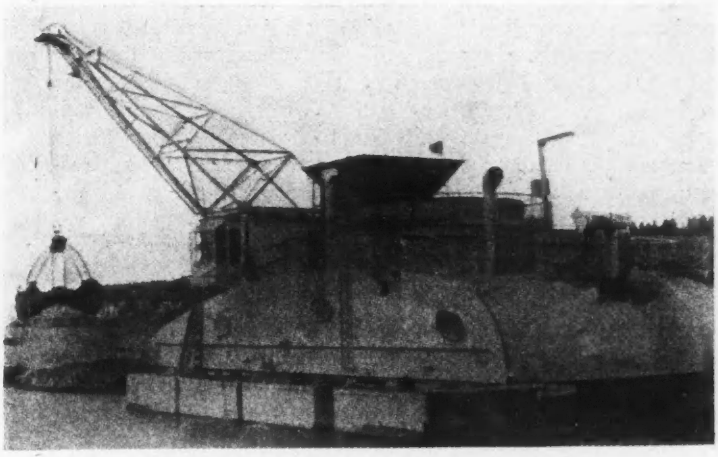


Fig. 2.—Washmill Mounted on a Barge.

during recent years. In dry-process kilns, especially those in Italy which have been put into operation during and since the war, the nodulisation of the raw material before being fed into the kilns has enabled the heat consumption to be reduced to 750,000 B.Th.U. per barrel of clinker (1050 kg.-cal. per kilogramme).

All the foregoing paragraphs are abstracted from "Rock Products."

Strengths of Italian Cement.

The adverse effect of war-time conditions on the quality of Italian cement and the subsequent rapid improvement is shown by data given in a report in "Ricerca Scientifica e Ricostruzione." Considering the compressive strength at 28 days as the standard, the percentage of cement attaining or exceeding the specified strength for neat cement specimens was only about 6 per cent. in 1945, 15 per cent. in 1946, and 52 per cent. in 1947. Probably owing to the difficulty

of obtaining suitable sand for cement testing, in addition to the unsuitability of the fuels, the corresponding values for mortar tests were about 3 per cent., 4 per cent., and 22 per cent. The mean resistances were less than the high specified strength of 7112 lb. per square inch by 26 per cent., 11 per cent., and 9 per cent. for the years 1945, 1946, and 1947 respectively. The percentages of test results less than 4978 lb. per square inch at 28 days were 45 per cent. in 1945, 16 per cent. in 1946, and 4 per cent. in 1947. The figures for 1947 relate to the first eight months of that year and it is expected that the rapid improvement in strength since 1946 will be continued so that standard strengths are now possibly invariably attained or exceeded.

Bauxite in Hungary.

Although most of the bauxite mined in Hungary is exported either as raw material or as alumina for the manufacture of aluminium, the existence of large deposits may foster the production of high-alumina cement in Hungary and neighbouring countries. Bauxite was first discovered in Hungary in the Transylvanian mountains in the early 1900's, and these deposits were exploited by the Germans in the war of 1914–1918, when bauxite from France was unobtainable. These deposits are now more or less exhausted. In the early 1920's bauxite was discovered near Halimba, west of the Danube, and like that in France, Italy, and Yugoslavia, is found in conjunction with dolomitic rocks and limestone. The largest deposits are west and north of the Danube and the present total capacity is estimated to be about 270,000,000 tons. About 10 per cent. of this quantity is suitable for the production of alumina by the Bayer and similar processes, but with the development of new methods poorer qualities may be suitable. The original Bayer process required that the difference between the aluminium content and twice the silicon content of dried bauxite should be at least 52. To-day the quality of bauxite is expressed by the ratio of the aluminium content to the silicon content. If this ratio exceeds ten the Bayer process can be used. In the case of 10 per cent. of Hungarian bauxite the ratio is greater than 12, and in more than half it is from 5 to 10. In 1943 the world production of bauxite was estimated to be 7,000,000 tons, but is now about one-third of this amount of which, according to a recent report from which the foregoing is abstracted, Hungary produced one-seventh.

At an early date a method was developed in Hungary for the manufacture of bauxite-cement bricks, which were made by finely grinding a mixture of bauxite and chalk, pressing it into bricks, and firing the bricks in a furnace at a temperature of 1200 deg. to 1400 deg. C. This method has been improved by firing in an atmosphere rich in oxygen. The sintered bricks are ground to produce high-alumina cement.

The Cement Industry in Spain.

In the first volume of "Aglomerados de Hormigón Hidráulico," by Sr. P. Palomar, published in Spain, an account is given of the cement industry in Spain and the recent modifications to the standards for slag-cement are described. There are twenty-eight large cement works in the country, the annual productive capacity being about 2,800,000 tons, most of which is Portland cement. The con-

sumption of cement to-day in Spain is said to be at the rate of about 2 cwt. per inhabitant each year, the corresponding weights in 1939 being about ¾ cwt. in Spain, 3⅜ cwt. in Britain, 4 cwt. in Germany, 6 cwt. in Belgium, and 2 cwt. in France. The following paragraphs are translated from the same source.

High-alumina Cement in Spain.

Most kinds of artificial cements are made in Spain, including a pozzolana cement (using native pozzolana) and high-alumina cement. The high-alumina cement contains about 40 per cent. of Al_2O_3, 8 per cent. of SiO_2, 11½ per cent. of Fe_2O_3 and 38 per cent. of CaO. The final set occurs in less than four hours. The residue on a sieve having 178 meshes per inch is 6 per cent. This cement has been made at Pallejá since 1928 with bauxite imported from France, but now bauxite found in Spain is also used. The compressive strength of 1:3 mortar at twelve hours is 7500 lb. per square inch, and nearly 9000 lb. per square inch at one day.

Zumaya Cement.

Another special cement, Zumaya cement, having a high degree of resistance to attack by sea-water, is used for marine work in northern Spain. In the specification for cements supplied for public works this cement is described as a quick-setting natural cement obtained by the calcination of a marl having the following percentage composition: SiO_2, 17·5 to 23; Fe_2O_3, 1·5 to 3; Al_2O_3, 6·5 to 11; CaO, 33·5 to 37; MgO, not more than 1·5. The marl is calcined with 6 cwt. to 7 cwt. of fuel of specified properties to each ton of cement produced. Zumaya cement must contain not more than 3·5 per cent. of SO_3 and 1·5 per cent. of MgO, and the loss on ignition must not exceed 10 per cent. Setting must commence between three minutes to fifteen minutes after mixing with water and must end within five to 25 minutes. The residue on a sieve having 178 meshes per inch must not exceed 34 per cent., 17 per cent. on 76 meshes per inch, and 4 per cent. on 45 meshes per inch. Minimum tensile strengths of neat cement briquettes cured in air are 113 lb. per square inch at seven days and 142 lb. per square inch at 28 days. The corresponding minimum compressive strengths are 498 lb. and 569 lb. per square inch. Slightly lower strengths are required for specimens cured in water.

Spanish Regulations for Metallurgical and Blastfurnace Cement.

The requirements of the official specifications issued in 1930 for slag-cements were superseded in 1946 by a new specification in which metallurgical ("siderúrgico") Portland cement is defined as a product obtained by mixing granulated blastfurnace slag with Portland cement clinker in the proportions of not more than 30 per cent. of slag and not less than 70 per cent. of clinker. The SO_3 and sulphide contents must not exceed 3 per cent. and 1 per cent. respectively; the loss on ignition must not exceed 5 per cent, and added foreign matter 1 per cent.

Blastfurnace Portland cement ("cemento Portland de alto horno") contains 31 per cent. to 85 per cent. of slag, and 15 per cent. to 69 per cent. of Portland cement clinker. The maximum amounts of constituents are: SO_3, 4 per cent.;

sulphide, 1·4 per cent.; CaO, 55 per cent.; foreign matter, 1 per cent.; the loss on ignition must not exceed 5 per cent.

The maximum permissible residues of both types of cement are 16 per cent. on a sieve with 178 meshes per inch, and 1 per cent. on 76 meshes. The specific gravity must be at least 2·95. The initial and final setting times are 45 minutes and 12 hours respectively. The strengths are the same as required for Portland cement in the regulations of 1930. Methods for determining the sulphur and magnesia contents are described.

Water.

The Spanish regulations for the design and construction of public works require that water which is not potable must be analysed before being used for making or curing concrete to determine whether any impurity in the water may affect adversely the setting of the cement or the durability of the concrete. In particular the pH-value must not exceed 8 or be less than 6, the amount of sulphuric anhydride must not exceed 0·3 per cent., sulphide 0·5 per cent., and organic material 0·3 per cent., and the amount of sodium or magnesium chloride in water for use in reinforced concrete must not exceed 1 per cent. Carbohydrates in any quantity are prohibited.

Diseases in the Cement Industry.

SOME of the diseases to which workers in the cement industry are prone are discussed by M. Joseph Déforge in " Le Revue des Materiaux de Construction " for July 1948. The French laws apparently recognised cutaneous lesions as the only class of occupational malady caused by the action of cement for which compensation could be awarded. These skin diseases included primary dermatitis and pyodermatitis, and "cement itch" (eczematous secondary dermatitis). In the opinion of M. Déforge, there is practically no risk of silicosis in the manufacture of cement and lime. Silicosis is caused only by breathing air containing free silica in the form of a fine powder, which more or less petrifies the pulmonary tissues. In the manufacture of artificial cement the silica is hardly ever in an uncombined state.

In reporting in the " British Journal of Physical Medicine " on the occurrence of dermatitis in the asbestos-cement industry, Mr. Hindley-Smith states that this disease is prevalent only among men handling cement or a mixture of cement and asbestos, especially when wet, and that it is not caused by asbestos alone. Workers wearing rubber gloves are more susceptible, possible because heat and perspiration are predisposing factors, although by washing all cement from the inside of the gloves and by perforating the gloves to increase ventilation the deleterious effect was reduced.

Concrete in Atomic Research.

RADIOACTIVE isotopes are produced by the Ministry of Supply at the research establishment at Harwell, Berkshire, where two piles are in operation. The first pile is known as Gleep (graphite low-energy experimental pile) and was completed in August, 1947. It is designed to develop about 100 kw. as heat, and is used for the measurement of the properties of materials used in the construction of piles and for the production of isotopes. The second pile, Bepo (British experimental pile), is larger than Gleep, and is designed to develop 6000 kw. as heat in its uranium bars and, because of its much higher power, the intensity of radiation is correspondingly higher and greater precautions are taken to prevent the escape of the radiations. This pile is used for testing the structural and physical properties of materials to be used in future piles and will be the main source of isotypes.

The piles are surrounded by concrete shields, that around Gleep being 5 ft. thick and that around Bepo being slightly thicker. The thickness is a compromise between what can be constructed simply and what is required to secure the low degree of radiation outside the piles desirable for experimental work. The amount of radiation is also below the limit set by the Medical Research Committee. The shields are required primarily for neutrons and gamma-rays, and the conditions are not therefore comparable with protection against X-rays. The material of which the shield is made must have great density and a high atomic number for protection against gamma-rays, and a high hydrogen-content for shielding for neutrons. Lead, which is used for X-ray radiation, is therefore not suitable as it does not comply with the second condition, but ordinary structural concrete appears to be suitable for piles of low power and was used for Gleep. A barytes concrete was used for Bepo, and although there was some variation in the proportions of the constituents, depending on the supplies available, a typical mixture was 1 part of Portland cement, 1 part of barytes sand, 1 part of barytes flour, 3 parts of barytes pebbles, and 1 part of flint. The water-cement ratio was 0·65. Special cement was not necessary but barytes [a heavy spar (natural barium sulphate)] was used for the aggregate to obtain a concrete weighing nearly 220 lb. per cubic foot (density 3·5). No information is available for publication on the nuclear properties of concrete and cement mortar, or on the effect of continual exposure of concrete to nuclear radiation.

Cement Production in Brazil.

IT is reported that a new cement works is to be built in the Vale do Paraiba in which slag from the State steelworks at Volta Redonda will be used. Production is expected to start in two years. The Brazilian Council of Mines and Metallurgy estimates that one kiln at Volta Redonda would produce six million sacks of slag-cement a year. It is also reported that the output of the cement factory in the Belo Horizonte district is to be increased to 12,000 sacks a day, and that, if this is found to be sufficient to meet requirements, proposals to build two new cement works in the district may not be proceeded with.

Hydraulic Hardening of Portland Cement.

A CORRESPONDENT has raised the question of the use of the term "internal extraction" in our number for January 1948 in which we published an article by Professor Dr. Hans Kühl wherein are examined the two apparently opposed views of H. Le Chatelier (1887) and W. Michaelis (1893) on the process of the hydraulic hardening of cement. In the early years of the present century Michaelis described the process of setting as the production of a colloidal gel, hardening being attributed to shrinkage due to the progressive hydration of the unhydrated core of cement withdrawing from the gel the water required for hydration. This process Michaelis called "innere Absaugung," which can be expressed in English by "inner suction" (the term used by F. M. Lea and C. H. Desch in "The Chemistry of Cement and Concrete") or, less literally but probably more descriptively, by "internal extraction." The latter term, which is adopted in our translation of Professor Kühl's article, is used synonymously for "inner suction." We take this opportunity to correct the phrase "exhibit a light lime concentration" in line 19, page 9 of our number for January, 1948. This should read "exhibits a high lime concentration."

New Cement Factory in Sweden.

A NEW cement factory, with a capacity of 500 tons of clinker a day, has been built at Störä Vika, near Nynäshamn, Sweden, by the Skanska Cement A.B., and will start production early in the year 1949. The works, which has two kilns, cost £1,380,000.

New Cement Factory in Rhodesia.

A NEW cement factory at Colleen Bawn, between Beitbridge and Bulawayo, in Southern Rhodesia, built for Rhodesia Cement, Ltd., is expected to be in production early in 1949. The works will have an output of 100,000 tons a year, and provision has been made to double this capacity if required.

MISCELLANEOUS ADVERTISEMENTS.

SCALE OF CHARGES.

Situations Wanted, 3d. a word; minimum 7s. Situations Vacant, 4d. a word; minimum 10s. Box number 1s. extra. Other miscellaneous advertisements, 4d. a word: 10s. minimum.

Advertisements must reach this office by the 5th of the month of publication.

PATENT. The Proprietors of Patent No. 546933 for "Improvements in or relating to Cement" are desirous of entering into arrangements by way of licence or otherwise on reasonable terms for the purpose of exploiting the same and ensuring its full development and practical working in this country. All communications should be addressed in the first instance to Haseltine Lake & Co., 28 Southampton Buildings, Chancery Lane, London, W.C.2.

FOR SALE. Suffolk. Two sand and gravel pits, one comprising 22 acres freehold land, the other 20 acres leasehold, each self-contained in operation, for sale as going concerns including all plant, vehicles and equipment. Details from E. R. WHITLOCK, Surveyor & Auctioneer, Ipswich. Tel.: 4677.

SUPER REFRACTORIES for CEMENT KILNS

ALITE No. 1. 68% ALUMINA
Refractory Standard 3250° Fahr.

ALITE B. 57% ALUMINA
Refractory Standard 3180° Fahr.

ALITE D. 41% ALUMINA
Refractory Standard 3150° Fahr.

E. J. & J. PEARSON, LTD.,
STOURBRIDGE, ENG.

CEMENT
AND
LIME MANUFACTURE

Published by Concrete Publications, Ltd., 14 Dartmouth Street, London, S.W.1

INDEX TO VOL. XXI, 1948

PAGE

Admixture for cement, A resinous 121
Alkalis on the phase composition of clinker, Effect of 105
Analysis by colorimetric methods, Rapid 97
,, of Portland cement, Spectrographic 29, 60
Argentina, The cement industry in 34
Atomic research, Concrete in 127

AUTHORS:

Abbott, W. E., M.Sc., F.R.I.C., on The rate of development of the compressive strength of concrete 69

Blondiau, Leon, on Expansion of cement measured by autoclave tests 111

Dahl, L. A., on Proportioning raw materials for Portland cement 1, 107
Ewbank, W. R., and R. H. Bogue on Effect of alkalis on the phase composition of clinker ... 105
Hendrickx, M. J., on Technical advances in cement burning 82

Kühl, Professor Dr. Hans, on Hydraulic hardening of Portland cement 1

Lenhart, W. C., and N. C. Rockwood on New process in lime manufacture 25

Murdock, L. J., M.Sc., Ph.D., A.M.Inst.C.E., on The determination of the proportions of concrete 91

Pintor, M., on Test of pozzolana cement 83
Purdon, A. O., B.Sc., A.R.I.C., on The suitability of blastfurnace slag for the manufacture of cement 19
Rebuffat, A., on Hydrolysis in Portland cement... 54

Autoclave tests, Expansion of cement measured by, by Leon Blondiau 111

Bauxite in Hungary 124
Blastfurnace cement, British standard for Portland 37
Blastfurnace cement, Spanish regulations for ... 126
Blastfurnace slag for the manufacture of cement, The suitability of 19
Brazil, Cement production in 127
Brazilian standard for Portland cement 63
Briquette suitable for several tests, A cement ... 21
Britain, The cement industry in 87
Bulgarian standard for Portland cement 64
Bulk, Containers for cement in 86
,, Transport of cement in 121
Burning, Technical advances in cement 82
Chemistry of Portland cement 47
,, of Portland cement, Recent research on the 30

PAGE

China, The cement industry in 35, 106
Clay, Mechanical excavation of 24
Clinker, Additions to 22
,, Effect of alkalis on the phase composition of 105
Colorimetric methods, Rapid analysis by 97
Concrete, Determination of the proportions of, by L. J. Murdock 91
,, Durability of 62
,, Rate of development of the compressive strength of, by W. E. Abbott 69
Controls in lime manufacture, Automatic 61
Czechoslovakia, New specification for Portland cement in 15

Despatching cement from a riverside works, Packing and 32
Diseases in the cement industry 126
Dry process plants 123

Elutriator, A Swiss 78
Excavation of clay, Mechanical 24
Expansion of cement measured by autoclave tests, by Leon Blondiau 111

Fineness, Methods of measuring 78
Finland, The cement industry in 96
Flotation plant in Scandinavia 122
Fluid-solid catalyst process in lime manufacture ... 25
Fraction-defective charts for the control of the quality of cement 23

Gauging solutions 23
German cement industry 49
,, cement-making plant 109
,, cement patents 104
Germany, Cement from 110

Hardening of Portland cement, by Dr. Hans Kühl... 1
,, of Portland cement, Hydraulic 128
High-alumina cement, British standard for 37
,, cement in Spain 125
Hungary, Bauxite in 124
Hydraulic hardening of Portland cement ... 1, 128
Hydrolysis in cement, Research on 54

India, The cement industry in 84
Iraq, New cement works in 85
Italian cement, Strengths of 122

Japan, The cement industry in 85

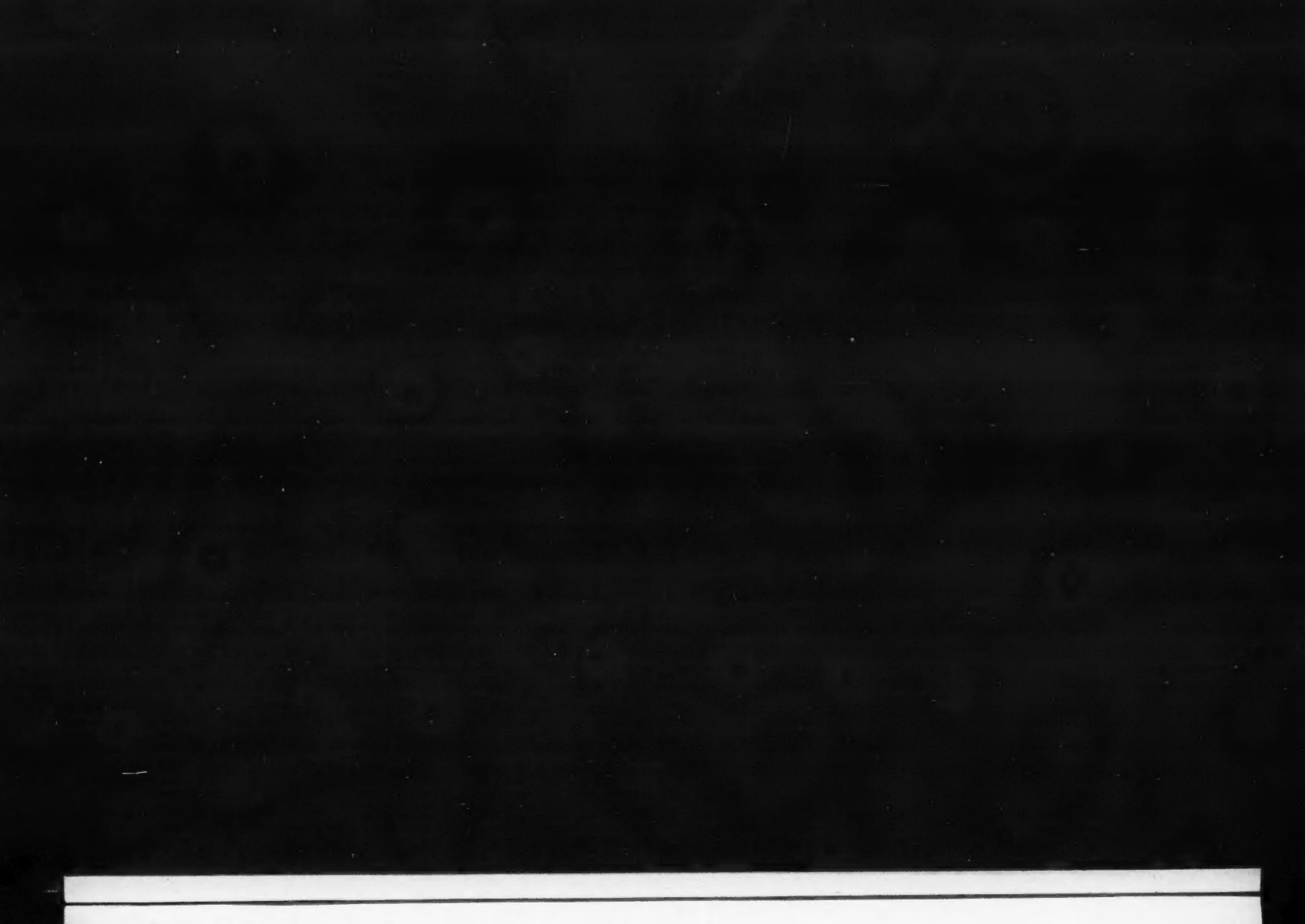
Kiln, Exceptional performance of a 120
Kiln preheaters... 123

	PAGE
Laboratory in the United States, A new	75
Lime in Portland cement, Formula for determining the amount of	15
,, manufacture, Automatic controls in	61
,, manufacture, New process of	25
Low-heat cement, Portuguese standard for	64
,, Portland cement, British standard for ...	37
Magnesia in cement	81
Metallurgical cement, Spanish regulations for ...	127
Mortar, Ready-mixed	16
,, test cubes, Machine for compacting	51
Packing and despatching cement from a riverside works	32
Patents, German cement	104
,, relating to cement, British	22
Poland, The cement industry in 35,	62
Portuguese standard for low-heat Portland cement...	64
Pozzolana cement, Tests on	83
Preheaters	123
Proportioning raw materials for Portland cement ...	107
Quality of cement, Charts for the control of the ...	23
Research on the chemistry of Portland cement, Recent	30
Resinous admixture for cement	121
Rhodesia, New cement factory in	128
Scandinavia, Flotation plant in	122
Slag for the manufacture of Portland cement, The suitability of	19
Slurry, Measuring the viscosity of	122
Soundness, The hot test for	74
Spain, Cement production in	85
,, High-alumina cement in	125
,, The cement industry in...	124
Spain, Regulations for metallurgical cement in ...	125
Specifications (see Standards)	
Spectrographic analysis of Portland cement ... 29,	60
Standard for high-alumina cement, British	37
,, for low-heat Portland cement, British ...	37
,, for low-heat Portland cement, Portuguese	64
,, for Portland cement, Brazilian	63
,, for Portland cement, British	36
,, for Portland cement, Bulgarian	64
,, for Portland cement, Czechoslovakian ...	15
,, for Portland cement, Uruguayan	66
,, for Portland cement, United States ...	108
,, for Portland blastfurnace cement, British...	37
Sweden, New cement factory in	128
Test cubes, Machine for compacting mortar	51
,, for soundness, The hot	74
Tests, A cement briquette suitable for several ...	21
,, Expansion of cement measured by autoclave, by Leon Blondiau	111
,, of pozzolana cement	83
Transport of cement in bulk 86,	121
Turbidimeters in Luxembourg, New types of ...	79
United States, Cement production in the	77
,, standard for Portland cement, Revision of the	108
,, Trends in cement manufacture in the	77
Uruguay, Standard for Portland cement in	66
Washmill, A floating	122
Water for concrete making	126
Zumaya cement	125

BOOKS ON CONCRETE

"CONCRETE SERIES"

books deal with the design and construction of reinforced concrete, precast concrete, the manufacture and chemistry of cement and lime, and kindred subjects. A detailed catalogue will be sent on request.

CONCRETE PUBLICATIONS LIMITED,
14, Dartmouth Street, Westminster, S.W.1.

Printed in England by The Cornwall Press Ltd., Paris Garden, London, S.E.1.